Calculation of partial pressures for high pressure gas mixtures.

When preparing high pressure gas mixtures you must take into account the fact that gases under high pressure behave as real gases and not ideal ones. A correction factor for the compressibility of the gas must be included in the equations when calculating partial pressures. The general equation of state of an ideal gas that is used in partial pressure mixing, Boyle's law, states that the quantity \((P*V)\) is a constant at constant temperature. This equation must be corrected to address the behavior of real gases under high pressure. Thus the expression:

\[
P_1* V_1 = P_2* V_2
\]

needs a supplementary factor, the compressibility factor \(Z\). If \(Z\) is less than 1 gases can be more easily compressed than gases with \(Z\) values greater than 1. The equation of state now becomes:

\[
\frac{(P_1* V_1)}{Z_1} = \frac{(P_2* V_2)}{Z_2}
\]

The \(Z\) value for oxygen at 165 bar (2400 psi) and 20°C is 0.941. Using the above equation, a gas cylinder with a volume of 5.7 liters (~40 ft³ @ 3000 psig) filled with oxygen to 165 bar would contain the equivalent of 999.5 liters of oxygen at 1 atmosphere instead of 940.5 liters calculated by the use of Boyle's law.

An empirical model for calculating the different partial pressures in a gas mixture while taking into account the compressibility factor \(Z\) is presented below.

The following equations show the relationship between the corrected partial pressures \(p_{za}, p_{zb}, p_{zc}, \ldots, p_{zn}\) and the total compressibility factor of the gas mixture \(Z_{tot}\).

Symbols:
- \(P\) = final pressure of the gas mixture.
- \(p_{za}, p_{zb}, p_{zc}, \ldots, p_{zn}\) = corrected partial pressure of the gas.
- \(a, b, c, \ldots, n\) = concentration of the specific gas (%Gas/100).
- \(z_a, z_b, z_c, \ldots, z_n\) = compressibility factors of the different components at pressures \(a*P, b*P, c*P, \ldots, n*P\).
- \(Z_{tot}\) = compressibility factor for the gas mixture, and
- \(Z_{tot} = (a * z_a) + (b * z_b) + (c * z_c) + \ldots + (n * z_n)\)
- \(p_{za} = (a * Z_{tot}) / Z_{tot}\)
- \(p_{zb} = (b * Z_{tot}) / Z_{tot}\)
- \(p_{zc} = (c * Z_{tot}) / Z_{tot}\)

Example:
A "Trimix" gas mixture with three components 21% \(O_2\), 35% He and 44% \(N_2\) was mixed using xxx's Law (Ideal Gas Equation of State). The total pressure \(P\) is 3000 psig and the partial pressures (and gauge readings) are given by:

\[
\begin{align*}
p_a & = (0.21 * 3000) = 630 \text{ psig} \\
p_b & = (0.35 * 3000) = 1050 \text{ psig} \\
p_c & = (0.44 * 3000) = 1320 \text{ psig}
\end{align*}
\]
The compressibility factors (the values in the Z factor table) of each gas at these partial pressures are:

\[
\begin{align*}
  z_a &= 0.972 \text{ (O}_2) \\
  z_b &= 1.038 \text{ (He)} \\
  z_c &= 0.998 \text{ (N}_2) 
\end{align*}
\]

The total compressibility factor is determined:

\[
Z_{\text{tot}} = (0.21 \times 0.972) + (0.35 \times 1.038) + (0.44 \times 0.998) = 1.0065
\]

The real gas partial pressures are calculated from the equations described above:

\[
\begin{align*}
  p_a &= \frac{p_{za} \times 0.972}{1.0065} = 630 \text{ psig} \\
  p_b &= \frac{p_{zb} \times 1.038}{1.0065} = 1050 \text{ psig} \\
  p_c &= \frac{p_{zc} \times 0.998}{1.0065} = 1320 \text{ psig}
\end{align*}
\]

Rearranging and solving for each gas:

\[
\begin{align*}
  p_{za} &= \frac{1.0065 \times 630}{0.972} = 652 \text{ psi} \\
  p_{zb} &= \frac{1.0065 \times 1050}{1.038} = 1018 \text{ psi} \\
  p_{zc} &= \frac{1.0065 \times 1320}{0.998} = 1331 \text{ psi}
\end{align*}
\]

The resulting mix is actually (see Note below):

\[
\begin{align*}
  \text{O}_2 &= 21.7\% \\
  \text{He} &= 33.9\% \\
  \text{N}_2 &= 44.4\%
\end{align*}
\]

This brings up the question: "What gauge partial pressures would provide the desired mix of 21/35 @ 3000 psi." To determine this, the following equations from the example above will be used. (A simple to use spreadsheet that will calculate these values can be found Here).

The real gas partial pressures would need to be:

\[
\begin{align*}
  p_{za} &= \frac{1.0065 \times pa}{0.972} = 630 \text{ psi} \\
  p_{zb} &= \frac{1.0065 \times pb}{1.038} = 1050 \text{ psi} \\
  p_{zc} &= \frac{1.0065 \times pc}{0.998} = 1320 \text{ psi}
\end{align*}
\]

Which would be:

\[
\begin{align*}
  pa &= \frac{630 \times 0.972}{1.0065} = 608 \text{ psig} \\
  pb &= \frac{1050 \times 1.038}{1.0065} = 1083 \text{ psig} \\
  pc &= \frac{1320 \times 0.998}{1.0065} = 1309 \text{ psig}
\end{align*}
\]

**Note:** The calculated real gas partial pressures total more than 300 psig. To resolve the minor difference in total pressure, successive iterations are needed. (i.e. recalculate the total compressibility factor with the new percentages.) The difference in this example (3000 vs. 3001) is small enough that in practice (mixing in the garage) you will not be able to observe it.